ORGANIC MAGNETS

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Magnetic ordering, e.g., ferromagnetism, like superconductivity, is a property of a solid, not of an individual molecule or ion, and very rarely occurs for organic compounds. In contrast to superconductivity, where all electron spins pair to form a perfect diamagnetic material, magnetic ordering requires unpaired electron spins; hence, superconductivity and ferromagnetism are mutually exclusive.

The vast majority of organic compounds are diamagnetic (i.e., all electron spins are paired), and a relative few possess unpaired electrons (designated by an arrow, ↑) and are paramagnetic (PM), i.e., they are oriented in random directions. A few organic solids, however, exhibit strong magnetic behavior and magnetically order as ferromagnets (FO) with all spins aligned in the same direction. In some cases the spins align in the opposite direction and compensate to form an antiferromagnet (AF). In some cases these spins are not opposed to each other and do not compensate and lead to a canted antiferromagnet or weak ferromagnet (WF). If the number of spins that align in one direction differs from the number of spins that align in the opposite direction, the spins cannot compensate and a ferrimagnet (FI) results. Metamagnets (MM) are antiferromagnets in which all the spins become aligned like a ferromagnet in an applied magnetic field. Above the ordering or critical temperature, T_c, all magnets are paramagnets (PM). Organic magnets all possess electron spins in p-orbitals, but these may be in conjunction with metal ion-based spins.

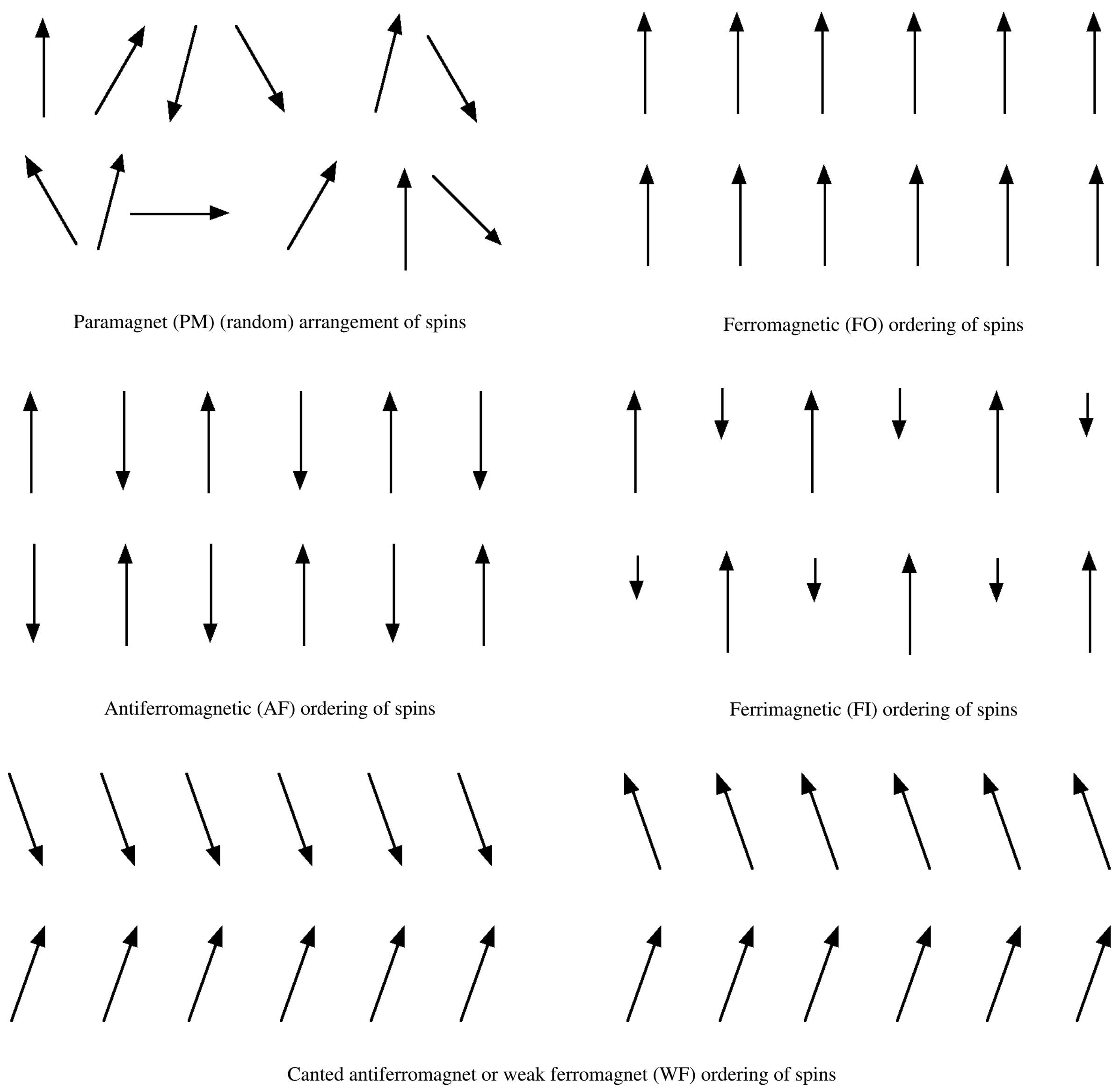


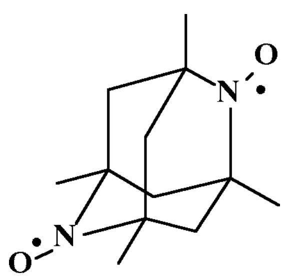
FIGURE 1. Schematic illustration of the different types of magnetic behavior.

Summary of the Critical Temperature, T_c, Saturation Magnetization, M_s, Coercive Field, H_{cr}, and Remanent Magnetization, M_r, for Selected Organic-Based Magnets

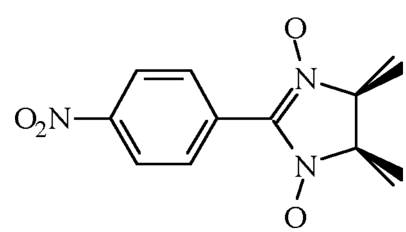
Magnet	Type	T_c/K	M_s/A m^{-1}	H_{cr}/T	M_r/A m^{-1}
α-1,3,5,7-Tetramethyl-2,6-diazaadamantane-*N,N'*-doxyl	FO	1.48	48,300	<0.00001	—
β-2-(4'-Nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-*N*-oxide	FO	0.6	22,300	0.00008	<200
$\{Fe^{III}[C_5(CH_3)_5]_2\}$[TCNE]	FO	4.8	37,600	0.10	2,300
$\{Mn^{III}[C_5(CH_3)_5]_2\}$[TCNE]	FO	8.8	58,200	0.12	3,700
$\{Cr^{III}[C_5(CH_3)_5]_2\}$[TCNE]	FO	3.65	46,300	—	—
α-$\{Fe^{III}[C_5(CH_3)_5]_2\}$[TCNQ]	MM	2.55	34,200	—	—
β-$\{Fe^{III}[C_5(CH_3)_5]_2\}$[TCNQ]	FO	3.0	21,600	—	—
Tanol subarate	MM	0.38	20,700	—	—
$NCC_6F_4CN_2S_2$	WF	35.5	45	0.00009	—
$Mn^{II}(hfac)_2NITC_2H_5$	FI	7.8	39,400	0.03	27,600
$Mn^{II}(hfac)_2NIT(i\text{-}C_3H_8)$	FI	7.6	42,400	<0.0005	<420
$[Mn(hfac)_2]_3[\{ON[C_6H_3(t\text{-}C(CH_3)_3]_2NO]_2\}$	FI	46	24,400	—	—
[MnTPP][TCNE]$\cdot 2C_6H_5CH_3$	FI	13	18,400	2.4	10,300
V$[TCNE]_x.yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$)	FI	~400	28,200	0.0015 - 0.006	1,650
Mn$[TCNE]_x.yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$)	FI	75	52,000	0.002	270
Fe$[TCNE]_x.yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$)	FI	97	46,300	0.23	3
Co$[TCNE]_x.yCH_2Cl_2$ ($x \sim 2$; $y \sim 0.5$)	FI	44	22,000	0.65	—

List of Symbols and Abbreviations

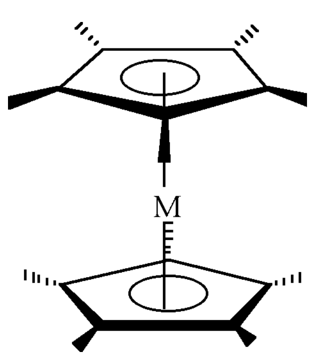
M_s	Saturation magnetization at 2 K	hfac	Hexafluoroacetonate
H_{cr}	Coercive Field	NIT	Nitronyl nitroxide
T_c	Critical Temperature	FO	Ferromagnet
M_r	Remanent magnetization at 2 K	FI	Ferrimagnet
TCNE	Tetracyanoethylene	MM	Metamagnet
TCNQ	7,7,8,8-Tetracyano-*p*-quinodimethane	WF	Weak ferromagnet



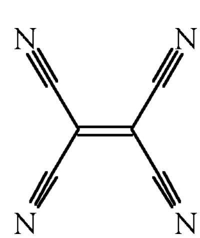
1,3,5,7-Tetramethyl-2,6-diazaadamantane-N,N'-doxyl



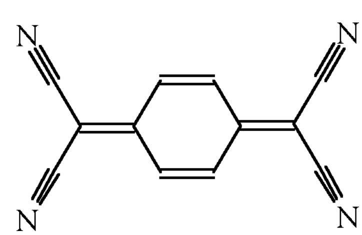
2-(4'-Nitrophyenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-*N*-oxide



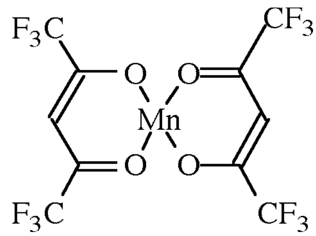
$M[C_5(CH_3)_5]_2$(M = Cr, Mn, Fe)



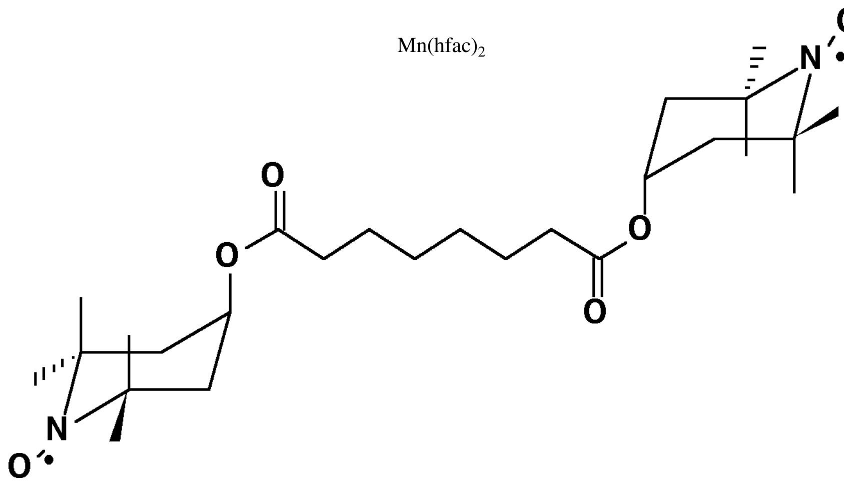
TCNE



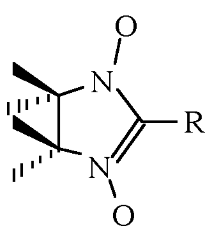
TCNQ



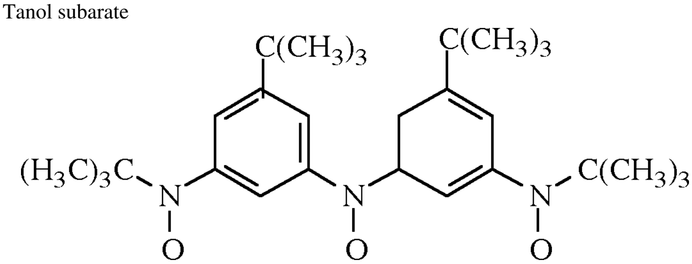
Mn(hfac)$_2$



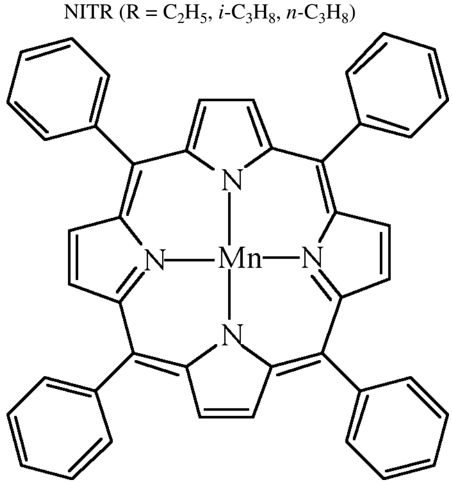
Tanol subarate



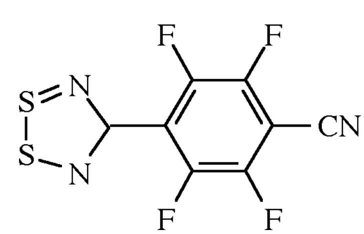
NITR (R = C_2H_5, *i*-C_3H_8, *n*-C_3H_8)



{ON[C_6H_3(t-C(CH_3)$_3$]$_2$NO]$_2$}



MnTPP



$NCC_6F_4CN_2S_2$

References

1. Miller, J. S. and Epstein, A. J., *Angew. Chem. Internat. Ed.*, 33, 385, 1994.
2. Chiarelli, R., Rassat, A., Dromzee, Y., Jeannin, Y., Novak, M. A., and Tholence, J. L., *Phys. Scrip.*, T49, 706, 1993.
3. Kinoshita, M., *Jap. J. Appl. Phys.*, 33, 5718, 1994.
4. Gatteschi, D., *Adv. Mat.*, *6*, 635, 1994.
5. Miller, J. S. and Epstein, A. J., *J. Chem. Soc., Chem. Commun.*, 1319, 1998.
6. Broderick, W. E., Eichorn, D. M., Lu, X., Toscano, P. J., Owens, S. M. and Hoffman, B. M., *J. Am. Chem. Soc.*, 117, 3641, 1995.
7. Banister, A. J., Bricklebank, N., Lavander, I., Rawson, J., Gregory, C. I., Tanner, B. K., Clegg, W. J., Elsegood, M. R., and Palacio, F., *Angew. Chem. Internat. Ed.*, 35, 2533, 1996.